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Czochralski growth and spectroscopic investigations of Yb^{3+}, La^{3+}:Na_2SO_4(I) and Nd^{3+}:Na_2SO_4(I)

Patric Mikhail, Reto Basler, and Jürg Hulliger[a)]
Department of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, CH-3012 Berne, Switzerland

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Ln^{3+}-stabilized Na_2SO_4 (phase I) single crystals were grown by the Czochralski method. Differential thermal analysis revealed the influence of the ionic radius of Ln^{3+} on the stabilization of Na_2SO_4(I). Distribution coefficients (~0.8–1.1) were measured by the inductively coupled plasma optical emission spectroscopy method and x-ray fluorescence spectroscopy. Spectroscopic investigations yielded absorption cross sections of 0.6×10^{-20} cm^2 (π-polarized, 928.5 nm) and 1.5×10^{-20} cm^2 (π-polarized, 797.3 nm) for Yb^{3+}, La^{3+}:Na_2SO_4 and Nd^{3+}:Na_2SO_4, respectively. Crystal growth of Gd^{3+}-stabilized Na_2SO_4(I) provides an interesting new material for stimulated Raman scattering experiments.

I. INTRODUCTION

The first Yb^{3+}-based solid-state lasers were demonstrated a long time ago.[1] In Yb^{3+} there are only two manifolds, the ground $^2F_{7/2}$ state and an excited $^2F_{5/2}$ state, which are separated by approximately 10,000 cm^{-1} (1 μm), which is also the typical laser wavelength of Yb^{3+} lasers. A narrow absorption band has made it inefficient to pump Yb^{3+}-doped crystals with broad band flashlamps, which were the only pump sources available in the 1960s and 1970s. The recent development of InGaAs laser diodes, showing narrow emission bands that almost match the absorption band of Yb^{3+}, led to an accessible pump source. The simple electronic structure of Yb^{3+} may therefore provide an advantage over other widely used activator ions such as Nd^{3+}, because two accessible electronic states preclude both upconversion and excited state absorption. Additionally, a small quantum defect can lead to high slope efficiencies[2] and low heat generation.[3] The emission lifetime of Yb^{3+} is larger than for Nd^{3+} by a factor of 3–4, if comparison is made for the same host.[4,5] Yb^{3+} lasers are expected to be quasi-four-level systems (300 K). The energy difference ΔE (around 200–600 cm^{-1}) is given by the terminal laser level above the ground state. Such an energy difference is comparable to the thermal energy present at room temperature (kT ~200 cm^{-1}): hence, the smaller the crystal field splitting, the more the terminal laser level is populated and therefore inversion population is more difficult to obtain.

With respect to new host lattices bearing a potential for laser applications, some new materials—e.g., M-fluorapatite [$M_5(PO_4)_3F$; M = Ca, Sr; fluorapatite (FAP), strontium fluorapatite (S-FAP), respectively][6–9] and Y– or Gd–calcium oxyborate [$MCa_4O(BO_3)_3$; M = Y, Gd][10–12] have recently attracted interest. Taking into account the potential of Yb^{3+} in particular host lattices, we have undertaken a broad search for new host materials, exploring at first the growth and the optical properties of Ln^{3+}-doped sodium sulfate (Na_2SO_4) phase I. Na_2SO_4 forms four crystalline modifications between room temperature and its melting point of 883 °C.[13–15] The hexagonal high temperature phase I[16] often occurs in $A_2(XO_4)$ compounds and changes into phase II spontaneously upon cooling; it is therefore not possible to obtain large single crystals of phase I at room temperature. However, Na_2SO_4 is known to allow for a wide range of solid solutions with different anions such as CO_3^{2-} and various cations.[17] The cations can be of uni-, bi-, or trivalent character, such as K^+, Ni^{2+}, Cu^{2+}, or Y^{3+}, including Ln^{3+} ions (La^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Yb^{3+}).[18–21] Phase I of Na_2SO_4 is stabilized by these ions and can therefore be preserved on rapidly cooling to room temperature without further structural modifications. However, for particular ions stabilization is possible by slow cooling, a condition that is necessary for obtaining crystals, which show no cracking during cooling and polishing. With the ability to from solid solutions of Na_2SO_4 and $Ln_2(SO_4)$, covering a wide range, it should be possible to achieve significant dopant concentrations of Ln^{3+} in the Na_2SO_4(I) lattice. Crystals of $Na_{2-3x}Ln_x\square_{2x}SO_4$ (Ln = La^{3+}, Nd^{3+}, Gd^{3+}, Yb^{3+}, or Y^{3+}; $\square$ = Na^+-vacancy) were grown by the Czochralski method. Characterization was performed by differential thermal

a)Address all correspondence to this author.
e-mail: juerg.hulliger@iac.unibe.ch

analysis (DTA), and absorption spectroscopy. We also report on the distribution coefficients of the doped species in the host of Na_2SO_4(I), measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) and x-ray fluorescence spectroscopy.

II. CRYSTAL GROWTH OF STABILIZED SODIUM SULFATE PHASE I CRYSTALS AND CHARACTERIZATION

Starting materials for crystal growth were Na_2SO_4 (phase V) (Fluka, anhydrous, 99.9%), metal sulfate hydrates (Aldrich, 99.9%) of La^{3+}, Yb^{3+}, Nd^{3+}, or Y^{3+} and $Gd_2(SO_4)_3$. The latter was prepared from Gd_2O_3 (Aldrich, 99.9%) by dissolving the oxide in a stoichiometric amount of 0.3 M sulfuric acid. Excess solvent was removed by heating to dryness at 80 °C. The resulting white crusted solid was washed with water, redissolved in water, and then recrystallized by heating slowly to obtain $Gd_2(SO_4)_3 \cdot 8H_2O$. The white powder obtained was filtered and washed with cold water once more before drying at 40 °C. Powder x-ray diffraction data of the obtained material are in agreement with reported data on $Gd_2(SO_4)_3 \cdot 8H_2O$.[22]

Powder mixtures were prepared by grinding Na_2SO_4 together with the metal sulfates in a mortar. The following compositions have been investigated: Y and Yb (2 and 1 mol%), Nd (3 mol%), Yb (5 mol%), Gd (3 mol%), Gd and Yb (5 and 1 mol%), and La and Yb (4 and 0.5 mol% or 3 and 1 mol%). Single crystals were obtained by using a resistively heated furnace. Growth was performed in porcelain (staatlich Berlin) or platinum crucibles. The melt was superheated for 5 h to achieve homogeneity. The crystals were grown on a Pt–Rh wire with a rotation speed of 30 rpm and at a pulling rate of 2.5 mm/h. For reasons of annealing, boules were kept another 24 h at 800 °C and then cooled down to room temperature at a rate of 35 °C/h. Typical crystals were about 20 mm long and 8 mm in diameter. The angle between the growth direction and the *c* axis of the hexagonal lattice turned differed from run to run. Because Na_2SO_4 is a hydrate-forming compound, crystals became coated with a white crust of a hydrous phase when stored in air for more than a few days. However, this should not give rise to serious handling problems, because the hydration reaction is slow. In this respect Na_2SO_4(I) shows a lower chemical stability than other materials mentioned above.[6–12]

III. RESULTS AND DISCUSSION

A. Melt stability and effects of dopants

According to the literature,[23] pure liquid Na_2SO_4 is reported to be stable up to temperatures of 1350 °C, but it shows a loss by evaporation of SO_3. Indeed, the analysis of the residue during our experiments showed a leak of sulfur, but the loss of material over 24 h at melting temperature was only about 2% of the total charge. Hence, thermally induced decomposition was not significant during the growth process.

For Na_2SO_4 stabilized by Nd^{3+} we could obtain transparent pinkish boules of optical quality as reported earlier.[21] However, all our efforts to stabilize the high-temperature phase of Na_2SO_4 by Yb^{3+} met with no success. Because of a phase transition during cooling we obtained cloudy crystals. In effect, we anticipated that coinclusion of Y^{3+} as a further component would stabilize the high-temperature modification of the host. Nevertheless, colorless opaque boules were produced. Note that the ionic radius of Y^{3+} (0.90 Å, CN:6) is almost the same as that of Yb^{3+} (0.87 Å, CN:6). The size of Y^{3+} and Yb^{3+} seemed to provide a possible answer to the difficulties in stabilizing phase I by these ions. Further efforts at stabilizing the host lattice by the inclusion of other Ln^{3+} with a radius more similar to Na^+ were finally successful. Gd^{3+} (CN:6), which is only 8% smaller than Na^+ (CN:6) led to colorless, transparent crystals of good optical quality when added to Na_2SO_4(I). This situation changed when Gd^{3+} and Yb^{3+} were simultaneously added, because cloudy crystals resulted again. At this point, it became clear that the Yb^{3+} introduced significant stress into the high-temperature modification of Na_2SO_4. Finally, when La^{3+} and Yb^{3+} were used (8:1, molar ratio) crack-free colorless, and transparent crystals of optical quality were obtained.

B. Distribution coefficients

Distribution coefficients were calculated from ICP-OES analyses (Varian Liberty 150 AX turbo emission spectrometer). The solvent for standards and the samples was 0.1 M, HCl except for Yb^{3+}, where a mixture of 0.4 M HNO_3 and 0.1 M HCl in a 1:1 ratio was used for both samples and standards. For comparison, x-ray fluorescence analyses were carried out. Samples were prepared by grinding 200 mg of the crystals and pressing the powder into a pellet. For excitation an Am-241 ring source was used and detection was done with a Si detector.

Table I shows the effective distribution coefficients resulting from the two methods. Obviously, the values for k_{eff} obtained by ICP and x-ray fluorescence do not match. It remains unexplained why for ICP measurements no reproducible values could be obtained for Yb^{3+}. In the case of Yb^{3+}, a matrix or solvent effect may eventually be responsible for deviations found in different series of measurements. Despite some difficulties in precise determination of k_{eff} values, we recognize that because of the general ability of Na_2SO_4 to form solid solutions, the distribution coefficients are significantly larger for Na_2SO_4 than in typical laser host materials.

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C. Differential thermal analyses

DTA measurements were carried out with a Mettler Toledo system. Samples (15–30 mg) were prepared in a Pt-Pan. All studies were performed under an airflow of 50 ml/min with a heating rate of 10 °C/min. Because it is possible to stabilize M^{n+}:Na_2SO_4(I) down to room temperature within a wide range of composition, it remained an open question why, in the case of $M^{n+} = Yb^{3+}$, phase I could not be stabilized. Results are presented in Fig. 1. Only thermograms of the solid solutions containing (i) Gd^{3+} or (ii) Nd^{3+} including those of (iii) La^{3+} (codoped with Yb^{3+}) showed no indication of a phase transition between room temperature and melting (endothermic signal at ~900 °C). The occurrence of the hexagonal phase (I) was confirmed by single crystal or powder x-ray analysis at room temperature. This may be a clue that such samples are truly stabilized phases, which can be stored at room temperature and do not undergo a segregation in a dry atmosphere. The observed thermal stability is in good agreement with the full transparency of these samples. However, Na_2SO_4 doped by (i) Y^{3+} plus Yb^{3+}, (ii) Gd^{3+} plus Yb^{3+}, or (iii) Yb^{3+} showed an endothermic peak in the range 270 °C to 360 °C. These signals monitor a phase transition from the hexagonal phase I to a monoclinic phase described by Eysel *et al.*[19] These observations are confirmed by our single crystal and powder x-ray analyses.[24] In contrast, there was no evidence for a monoclinic phase in undoped Na_2SO_4. On the basis of published phase relationships,[14] the signal at ~280 °C for undoped Na_2SO_4 belongs to the III ⇌ II and II ⇌ I phase transitions, because on cooling phase I changes into orthorhombic Na_2SO_4(II), followed by a change into the metastable orthorhombic Na_2SO_4(III) phase, separated by a ΔT of about 7 °C. The stability of Na_2SO_4(I) containing La^{3+} and Yb^{3+} is described elsewhere.[25] On the other hand, Nd^{3+} and Gd^{3+} doped crystals seem to gain stability due to similar ionic radii of the dopants compared with Na^+. For a coordination number of 6, Nd^{3+} and Gd^{3+} ionic radii match that of Na^+ up to 96% and 92%, respectively. Yb^{3+} obviously is too small to stabilize phase I of Na_2SO_4 [missmatch in ionic radii with respect to Na^+: 15% (CN:6)]. Eysel *et al.*[19] reported stabilization of Na_2SO_4(I) by Y^{3+} [missmatch in ionic radii with respect to Na^+: 12% (CN:6)] when quenching crystals from high temperature. In our case, slow cooling of Y^{3+}-doped Na_2SO_4 produced cloudy and twinned crystals not featuring phase I.[25]

TABLE I. Distribution coefficients k_{eff} for Y^{3+} and different Ln^{3+} in Na_2SO_4(I) measured by ICP and x-ray fluorescence spectroscopy. (+Yb) indicates that samples were codoped with Yb^{3+}.

	Y	Gd	Gd (+Yb)	Nd	La (+Yb)	Yb
ICP	0.96	0.43	0.50	0.87	0.86	*
X-ray fluorescence	1.12	1.19	0.83	1.07	1.03	0.9

*See text.

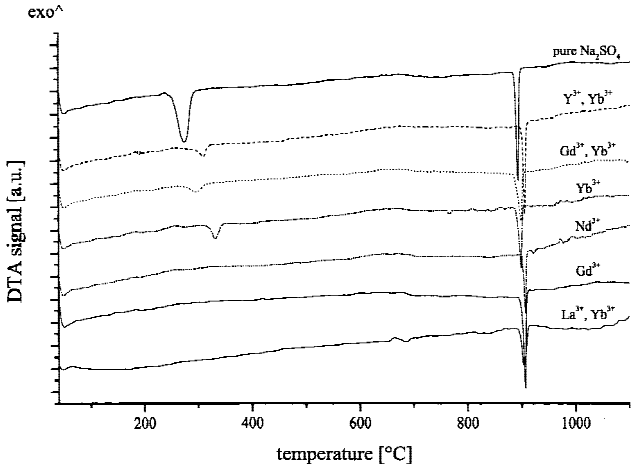

FIG. 1. DTA curves of pure and doped Na_2SO_4 crystals. Na_2SO_4 containing Yb^{3+}; Gd^{3+} (codoped with Yb^{3+}) and Y^{3+} (codoped with Yb^{3+}) exhibit a phase transition between 270 and 360 °C (see text). These crystals were not transparent. Nd^{3+}-, Gd^{3+}-, and La^{3+}- (codoped with Yb^{3+}) stabilized crystals of optical quality showed no phase transition. The endothermic signals of ~900 °C correspond to melting. Signals occurring (i) at ~650 °C for samples stabilized by La^{3+} (codoped with Yb^{3+}) and (ii) at ~730 °C for crystals stabilized with Yb^{3+} cannot be attributed to known phenomena of these materials. These signals may be due to relaxation of stress.

D. Optical properties

Spectroscopic investigations were carried out with a Cary 5E (Varian). Figures 2 and 3 show the absorption spectra of La^{3+}, Yb^{3+}-codoped Na_2SO_4(I) and Nd^{3+}-

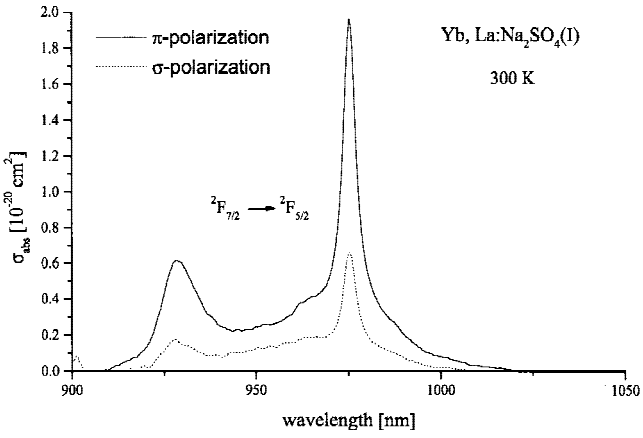

FIG. 2. Absorption spectrum in π and σ polarization of La^{3+}-stabilized hexagonal Na_2SO_4(I) doped with 0.5 mol% Yb^{3+}.

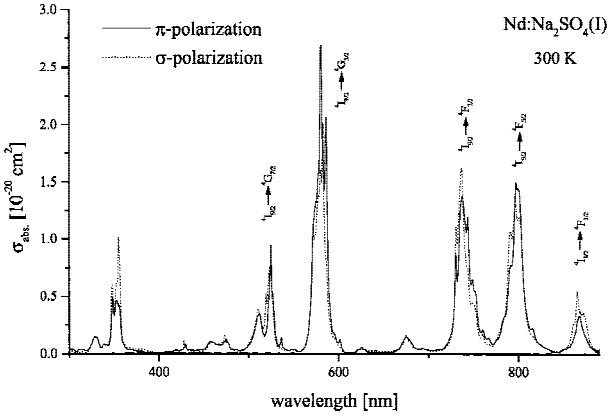

FIG. 3. Absorption spectrum in π and σ polarization of Nd^{3+}-(3 mol%) doped hexagonal Na_2SO_4(I).

doped Na_2SO_4(I) single crystals at room temperature. Because of difficulties in measuring a precise dopant concentration in Na_2SO_4 crystals, for calculation of the absorption cross sections we presume that the distribution coefficients of Yb^{3+} and Nd^{3+} are close to 1. If the effective distribution coefficients are <1, the absorption cross sections will be corrected to larger values than the lower limits given here. The absorption cross section of Yb^{3+} at 928.5 nm was estimated to be 0.6×10^{-20} cm^2 (π polarization). This is almost as large as Yb:yttrium–aluminum–garnet (YAG) (0.8×10^{-20} cm^2 at 940 nm).[26] The absorption cross section of Nd^{3+} in Na_2SO_4(I) of 1.5×10^{-20} cm^2 (797.3 nm, π-polarization) was about a factor of 5 smaller than in Nd:YAG (7×10^{-20} cm^2 at 808 nm).[27]

IV. CONCLUSIONS

Crystal growth of Na_2SO_4 phase I doped with various Ln^{3+} ions has produced a new material for optical applications. We have obtained (i) Nd^{3+}-, (ii) Gd^{3+}-, and (iii) La^{3+}- plus Yb^{3+}-doped crystals of optical quality and thermal stability. Because phase I of Na_2SO_4 slowly degrades in wet air, crystals must be kept in a dry atmosphere for all optical experiments. A rather large k_{eff} allows for efficient doping and therefore stabilization of slowly cooled crystals of large size. Absorption cross sections of Yb:Na_2SO_4 are similar to those obtained in Yb:YAG. As demonstrated recently,[28] inorganic lattices providing molecular type ions such as NO_3^-, ClO_3^- and SO_4^{2-} are of interest to stimulated Raman scattering (SRS) laser emissions. Recently we demonstrated a nanosecond Raman laser at 1.1628 μm by using for the first time a $NaBrO_3$ crystal.[29] In this respect, Gd^{3+}-stabilized Na_2SO_4(I) represents a promising new SRS material. In the case of Na_2SO_4 phase V we have already obtained effective Stokes and anti-Stokes SRS frequency conversions.[30] Growth and characterization of Gd^{3+}-stabilized Na_2SO_4(I) is in progress. [While this paper was being reviewed, we succeeded in growing 5.2 cm (Ø = 1.7 cm) single crystals of Gd^{3+}:Na_2SO_4(I) of high optical quality showing strong SRS responses.[31]]

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